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Research Paper

NANO-CLAY COMPOSITE AND PHYTO-NANOTECHNOLOGY: A NEW HORIZON TO FOOD SECURITY ISSUE IN INDIAN AGRICULTURE

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Abstract

The article represents the different and unique utilization of nano-clay polymer composite and Phyto-nanotechnology, to achieve the goal of food and nutritional security and safety in India. These emerging technologies can be proved as powerful candidates for enhancing nutrient use efficiency, upgrading activity and efficacy of bioagents and PGRs and regulating use of agrochemicals in field. In a nut shell, how these nano-integrated strategies would obviously strengthen the backbone of rainfed agriculture that occupied significant cropped area and how would tide over the hurdles of climate change and promote the productivity issue in Indian agriculture is described here. The other aspect of this article is to portray the processes of green or organo-manufacturing of NP and NMs by Phytonanotechnology and clay polymer composites. Because this benign approaches not only will diminishes the risks of eco toxicity but also opens up enormous scope for employing nanotechnology in Indian agriculture.
Key words: Phyto-nanotechnology, Nano-clay composite, PGR, Rainfed agriculture.

INTRODUCTION

Indian agriculture is engulfed with wide spectrum of challenges such as stagnation in crop yields, low nutrient use efficiency, declining soil organic matter, multi-nutrient deficiencies, climate change, shrinking arable land and water availability, heavy metal contamination of soil and water etc. (ground water in Malwa belt of Punjab has uranium metal that is 50% more than trace level, Ranipet area, Agra are cursed with Pb, Cd pollution, Uttar Pradesh is facing problem of F pollution, major portion of West Bengal is contaminated with As). Phyto-nanotechnology that involves nano-matrics and green plants as a co-soldier, is a strong mean to address these constraints.

According to an encyclopedic source, nanotechnology is defined as the design, characterization, production, and application of structures, devices, and systems by controlling shape, size at the nano-scale (1-100 nm) and a high surface-volume ratio. Now phyto nanotechnology is growing and harvesting organic nano-particles from plants, or nano- particle decorated with organic clay material used in crop improvement or protection. It represents an important step in the development of nano-manufacturing, cost–effective technology that has vast and promising applications in agricultural aspects, such as use of nano-sensors for detection of soil quality and health, soil remediation by removing pollutants by reactive nano-magnet, photo-catalysis, stabilization of bio-pesticides with nano-structured absorbents, slow release of nano-material assisted fertilizers, bio-fertilizers, agrochemicals and micronutrients for efficient use, nano-material assisted delivery of genetic material, designing pheromone releasing fibers for crop protection etc. Zhu, J of the University of Queensland is researching carbon nanotubes (CNT) for trapping greenhouse gas emissions caused by coal mining and power generation. CNT can trap gases up to a hundred times faster than other methods, allowing integration into large-scale industrial plants and power stations. Oxidized and hydroxylated CNTs are good absorbers for metals such as Cu, Ni, Cd and Pb.

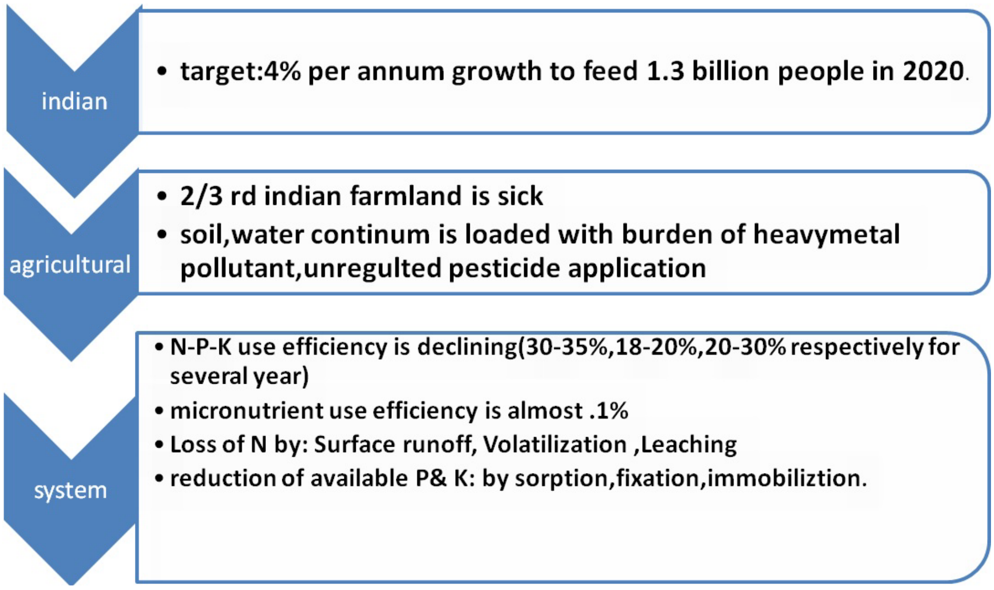


Fig 1: Depicting the challenges, and goals of Indian agriculture

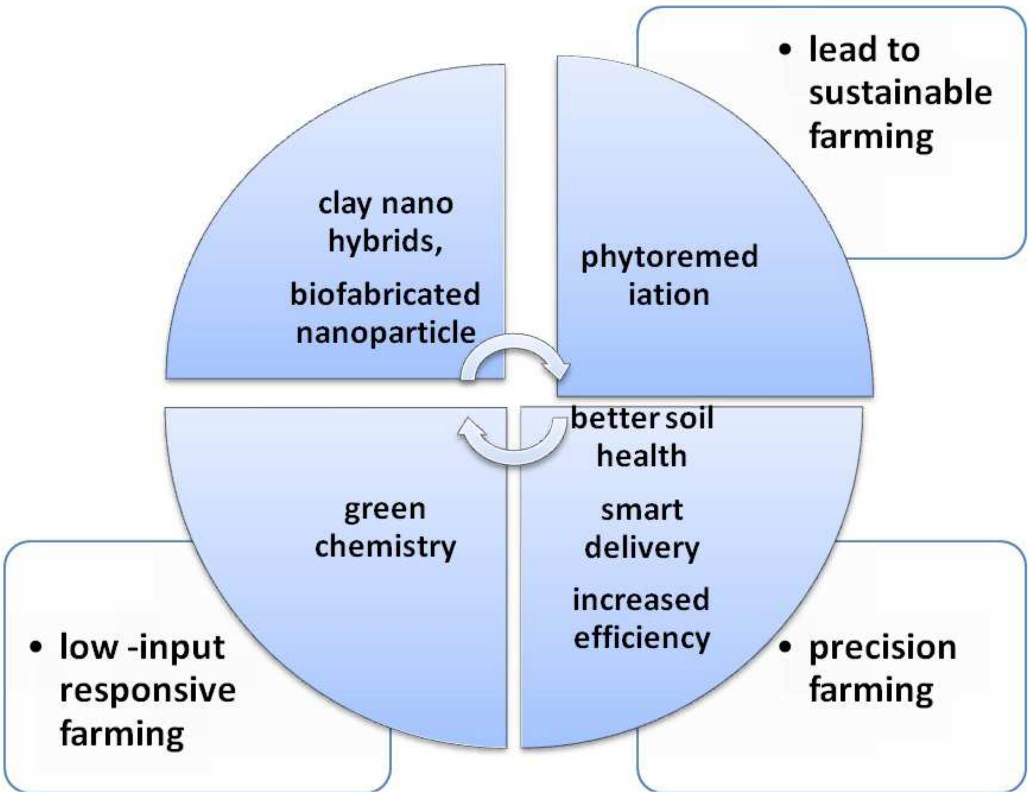
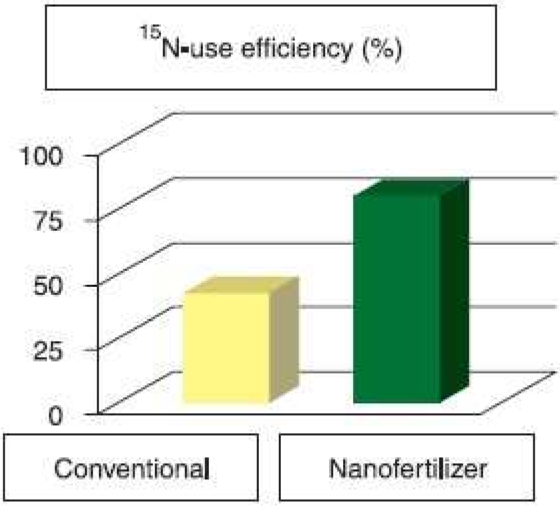


Fig 2: Advantages of nanotechnology in different sphere of agriculture

2. SOME FEEBLE LINKAGES OF INDIAN AGRICULTURE: CAN BE RESOLVED BY NANO-FORTIFICATION

2.1 Nanoclay –hybrid: A useful smart delivery system:

The world demand for fertilizer consumption is increasing day by day where as its use efficiency is declining. The nano-clay loaded with different fertilizer like N, P and K show the slow release due to intercalation of clay surrounding the polymer composite. In India, Bansiwal *et al. (2006)* developed a surface modified zeolite as a carrier of slow release phosphatic fertilizer. Liu *et al. (2006)* have shown that nano-composites containing organic polymer intercalated in the layers of kaolinite clays can be used as a cementing materials to regulate the release of nutrients from conventional fertilizers. Nano-fertilizers are capable of releasing nutrients, especially NO_3-N for more than 50 days as compared to conventional fertilizer (urea) which ceased to exist beyond 10-12 days (Subramanian and Rahale, 2000). The properties of nano-particles (more surface area) may help in increasing the reactive points of these particles and hence increase the reactivity of these nanoparticles. This leads to changes in the physio-chemical properties of these nanoparticles which help in the absorption of fertilizers in plants (Anonymous, 2009). The promoting effect of nano-particles on seedling growth and development were reported by Zhu et al. (2008). Also, nano-iron oxide com-paredto other treatments such as organic materials and iron citrate facilitated photosynthesis and iron transfer in peanut leaves (Liu et al., 2005).



Nitrogen-use efficiency (%) of conventional and nano-fertilizers

2.2 Nutritional security can be achieved by increasing micronutrient use efficiency

Essential nutrients are irreplaceable by other elements, which are directly involved in plant metabolism and without it, plant cannot compete their life cycle.The essential micronutrients are metals (except B and Cl) and its uptake is affected by soil (Lindsay, 1991; Stevenson, 1986; Lake *et al*., 1984), plant (Barber, 1995; Marschner, 1995) microbial and environmental factors (Romheld and Marschner, 1986; Clark and Zeto, 2000). In india, Sulphur has become critical on low organic matter coarse-textured soils. Zinc deficiencies are widespread across the country. Magnitude of boron deficiencies is also increasing. Manganese deficiencies are common on coarse textured Indo-Gangetic alluvial plains. At present about 48.1% of Indian soils are deficient in diethylene triamine penta acetate (DTPA) extractable zinc, 11.2% in iron, 7% in copper, 5.1% in manganese, and 11% Mo. Apart from the deficiency of these micronutrients, deficiencies of boron and molybdenum have also been reported in some areas. In areas with multi-micronutrient deficiencies, simple fertilizers are insufficient to exploit the potential of crops and cropping systems. Micronutrients serve mainly as constituents of prosthetic groups in metalloproteinase and as activators of enzyme reactions. (The function of micronutrients has been reviewed extensively by Marschner, 1986; Romheld and Marschner, 1991; Mortvedt *et al.,* 1991; Mortvedt 2000 and Fageria *et al.,* 2002). Soil factors like pH, organic matter content, cation exchange capacity (CEC), clay content, temperature and moisture affect the availability of micronutrients to crop plants. The accumulation of micronutrients varies among plant species and cultivars/genotypes within species (Marschner, 1995), which have been attributed by genetics, environment, physiological biochemical mechanism, response to agronomic management practices and tolerance to pest and diseases. The soil contains nutrients for the plant absorption, translocation and metabolism but bioavailability is very much less in case of several micronutrients as mentioned above. And this multi-micronutrient deficiency not only hampering plant growth and metabolism but indirectly fails to fulfill the requirement of micronutrients in human diet. More than 3 billion people of the world are anemic, 90% of them are in developing countries. Iodine deficiency is the leading cause of mental retardation in the world. Zinc deficiencies in pregnant women have been associated with child births. Supplementation and fortification of mineral nutrients appears to be a partial solution to the malnutrition problem. Biofortification through conventional breeding has so far proved to be of little or no significance (Misra *et al.,* 2004). However, it would require a person to eat more than 5 kg of any of these staples each day to meet the requirements for vitamin A and iron (AVRDC, 2004). Consuming few spoonfuls of fruits and vegetable are much more reasonable option for satisfying one's daily micronutrient requirements. Improving the micronutrient uptake mechanism by slow releasing nano fertilizer to produce micronutrient rich diet can play an important role in tackling the malnutrition.

2.3 Nano-strategies promote Rainfed agriculture mitigating menaces of climate change

The impact of indiscriminate human activity on greenhouse gas emission changes global climate patterns is almost certainly the most discussed issue of the first decade of the 21st century. It is causing an impending water crisis in the context of continued population growth and increasing water demand for agriculture, industrial and domestic use.

The most recent estimates put global rain-fed croplands at 1.75 billion hectares at the end of the last millennium, which are about 5.5 times the irrigated areas of the world (GIAM, 2006). India ranks first among the rainfed agricultural countries of the world in terms of both extent (86 M ha) and value of produce. In dry land regions climate is largely semi-arid and dry sub-humid with a short (occasionally intense) wet season followed by long dry season. Rainfall is highly unreliable, both in time and space, with strong risks of dry spells at critical growth stages even during good rainfall years. Inter-annual fluctuations are high due to monsoonal climate-characteristics. It is estimated that 15 M ha of rainfed cropped area lies in arid regions and receives less than 500 mm rainfall, another 15 Mha is in 500-700 mm rainfall zone, and bulk of 42 M ha is in the 750-1100 mm rainfall zone.

The last four decades of Indian agriculture registered impressive increase in food production, food security and rural poverty reduction in better endowed 'Green Revolution' regions , bypassed the less-favored rainfed areas which were not the partners in this process of agricultural transformation. Both national and international research at experiment stations, operational projects and demonstrations at farmers' fields (Kanwar, 1999) have conclusively shown that highest gain production was seen when in-situ/ ex-situ rainwater harvesting and its subsequent utilization in the field was made. Nano-clay can be vigorously utilized as water harvesting tool for improving productivity of dry lands because these have high absorbing capacity, water holding capacity. Among cereals, millets (pearl millet and finger millet) and maize, it is recorded that less than 30% increase in productivity is due to irrigation. So to bridge the gap of water requirement and optimum yield, nanoclay particle, nano- clay composites may be proved as efficient means.

2.4 Nano-sensors: a boon to combat abiotic and biotic stresses

Nanopesticides can increase the dispersion and wettability of agricultural formulations (i.e., reduction in organic solvent runoff), and unwanted pesticide movement (Bergeson, 2010). Nanomaterials and biocomposites exhibit useful properties such as stiffness, permeability, crystallinity, thermal stability, solubility, and biodegradability (Bouwmeester et al., 2009; Bordes et al., 2009) needed for formulating nanopesticide. Naturally, nanoparticles can be used as biomarkers or as a rapid diagnostic tool for detection of bacterial, viral and fungal plant pathogens (Boonham et al., 2008; Yao et al., 2009; Chartuprayoon et al., 2010) in agriculture, though this research is in preliminary stage. Nanoparticles based sensors might offer improved detection limits in detecting viral pathogens in plant (Baac et al., 2006). Nanoparticles can either be directly modified to be used for pathogen detection, or used as a diagnostic tool to detect compounds indicative to a diseased condition. Nano-chips are types of types of microarrays that contain fluorescent oligo capture probes through which the hybridization can be detected (López et al., 2009). Above nano-chips are known for their sensitivity and specificity in detecting single nucleotide changes of bacteria and viruses (López et al., 2009). Yao et al. (2009) utilized a fluorescence silica nanoparticles in combination with antibody to detect *Xanthomonas axonopodis* pv. *vesicatoria* that causes bacterial spot disease in Solanaceae plants, indicating a potential for nanoparticle application in disease detection. Singh et al. (2010) used nano-gold based immuno sensors that could detect Karnal bunt (*Tilletia indica*) disease in wheat using surface plasmon resonance (SPR). Particularly, research attempted to detect the disease using SPR sensor in wheat plots for seed certification and to establish plant quarantines. Research on pathogen detecting nanosensors for their in-field application would be highly valuable for rapid diagnosis and disease management.

Plants respond to different stress conditions through physiological changes. One such response is the induction of systemic defense, which is thought to be regulated by plant hormones: jasmonic acid, methyl jasmonate and salicylic acid. Wang et al. (2010) harnessed this indirect stimulus to develop a sensitive electrochemical sensor, using modified gold electrode with copper nanoparticles, to monitor the levels of salicylic acid in oil seeds to detect the fungi (*Sclerotinia sclerotiorum*). They successfully and accurately measured salicylic acid using this sensor. Research on similar sensors and sensing techniques needs to be expanded for detecting pathogens, their byproducts, or monitor physiological changes in plants nano particles and quantum dots (QD) have emerged as pivotal tool for detection of a particular biological marker with extreme accuracy.

2.5 Nano-clay encapsulation of bioagents and PGRs are excellent vehicle for plant protection

Adzmi et al. (2012) reported that there was a clear distribution of conidia of *Trichoderma hazarium* UPM40 loaded in Ca-alginate MMT clay. Nano clay coated bioagents can retain their activity for longer period as well as can serve other nutritional supplementation too. The NCPC loaded *Trichoderma sp*. or *Pseudomonas sp* can control several fungal nematode disease complex that occur in pulses due to moisture and nutrient deficiency in rainfed rabi crops.

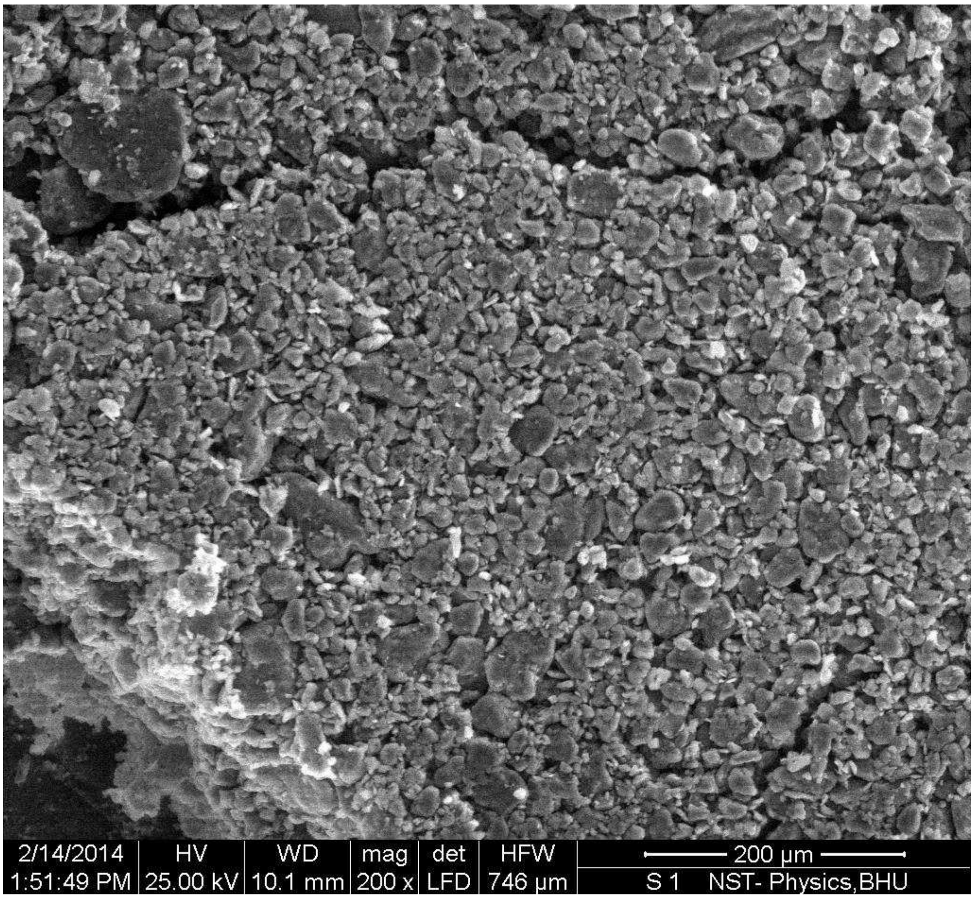


Fig 4: Bedillite based nano-clay polymer composite loaded with N, P and Trichoderma,

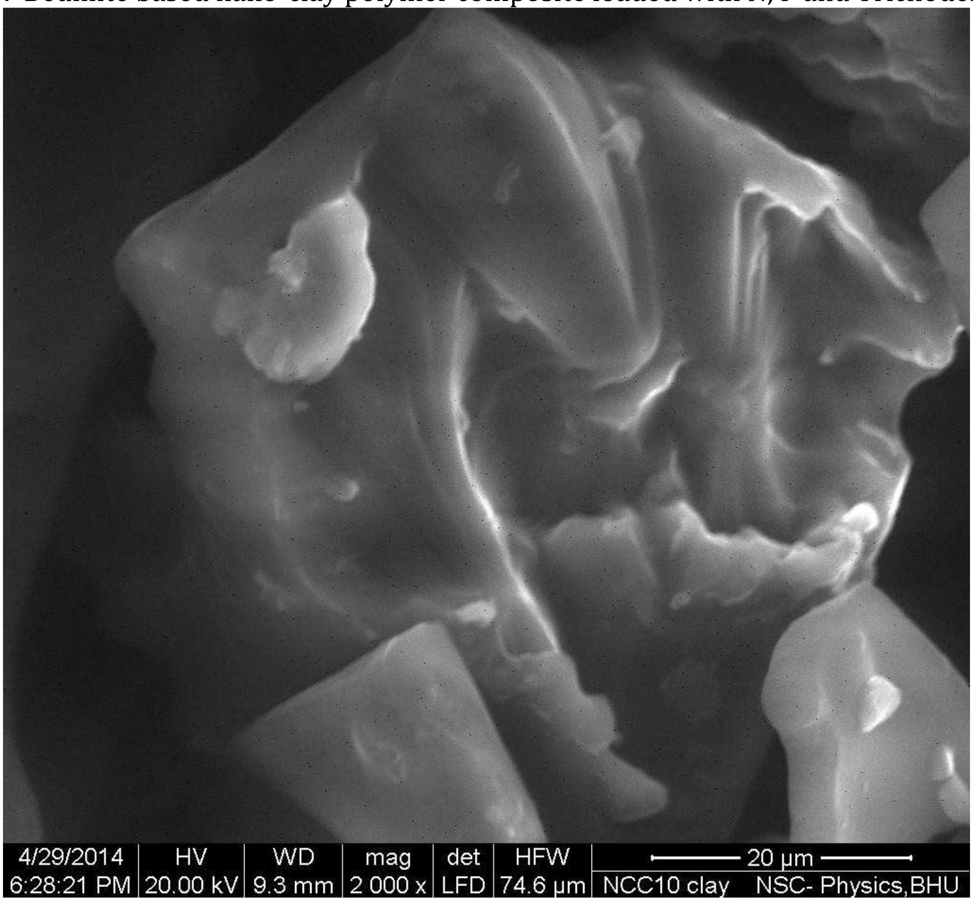


Fig 5: SEM of Bedillite based nano-clay polymer with *Trichoderma*

The new vermiculite-metallic copper hybrid material shows strong antibacterial activity against *Staphylococcus aureus* at 37 ^{0}C. Recently, metal nanoparticles such as those of copper and silver, which has broad spectrum antimicrobial activity have been conjugated with montmorillonite, kaolinite and sepiolite to increase their lifetime. According to a recent investigation on bactericidal effect of silver nanoparticles, the bactericidal properties of the nanoparticles are size dependent, with smaller particles (1–10 nm) resulting in better antibacterial efficiency. The NPs interact in the bacterial cell wall composition, or to genetic material and results in ROS production or hindrance in DNA replication or affect signal transduction eventually causing death.

2.6 Nanoclay polymer can enrich ecological health and quality of by decontamination

The nano size metal oxides and natural nano sized clays have been investigated for the removal of metals and inorganic ions. Soluble P, in the forms of phosphoric acid, phytic acid, and tri polyphosphate, has been examined for the sequestration of Cd, Cu, Pb, U, and Zn in contaminated environments & NPs containing these forms of phosphate is a unique complementary in-situ decontamination tool. Zero-valent iron is a new medium for waste water treatment and decontamination of soil. Nanoscale zerovalent iron (nZVI) i.e the elemental form of iron, and refers to the zero charge carried by each atom—a result of the outer valence level being filled, can reduce not only organic contaminants but also the inorganic anions nitrate, which is reduced to ammonia, perchlorate (plus chlorate or chlorite) and then reduced to chloride, selenate, arsenate, arsinite and chromate. The nZVI is also efficient in removing dissolved metals from solution, eg Pb and Ni. The reaction rates for nZVI are at least 25-30 times faster and also sorption capacity is much higher compared with granular iron. The metals are either reduced to zero valent metals or lower oxidation states, eg Cr (III), or are surface complexes with the iron oxides that are formed during the reaction. Thus this emerging tool can be used for improving quantity and quality of water and wastewater treatment system.

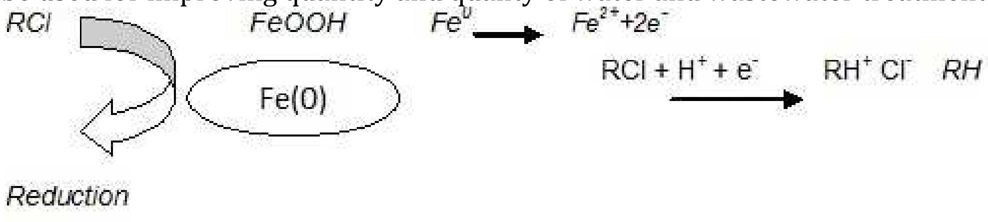


Fig 6: Dechlorination by nZVI.

Organoclays have proven to be the technology of choice for treating oily wastewaters (Speed et al 1987; Jasra et al 1999). Organoclays exhibit a synergistic effect with many commonly utilized water treatment unit processes including granular-activated charcoal, reverse osmosis, and air strippers. The experiment with *Panicum maximum* (Purple guinea grass) treated with different concentration of TNT and nZVI indicated that the combination between nanotechnology and phytotechnology for TNT remediation in contaminated soil resulted in higher accumulation of TNT in plant roots, particularly, the experiments with TNT concentration of 500 mg/kg. The study concluded that the TNT uptake by roots in nZVI added soil was more effective than that without nZVI. (Waraporn et al. 2013)

3. POSSIBLE BACKDROPS OF ADAPTATION OF THIS TECHNOLOGY

One cannot argue against the advantages of implication of nanotechnology but still some risk factors are waiting to be unveiled and examined. The toxic effects have been identified in taxes of fish and invertebrates that raise sufficient concern that NPs in the environment could have adverse effects on wildlife, if present at high enough levels. But as there are no biomarkers for NPs that could be used as part of a biological monitoring program it is very difficult to know the threshold concentration of NPs or NMs causing lethal effect. So whether this tiny technology bears any eco-hazard or not; this doubt is remained to be clarified with advance of time demanding great focus on research of ecotoxicity of NPs. Poland et.al. (2008) showed that multiwalled carbon nanotube (MWCNT) caused cancer in mice (Poland, 2008) and also damaged DNA in human lungs (Lindberg, 2009). High concentrations of some ENPs reduced plant growth and increased the permeability of bacterial cells (Doshi, 2008), NPs may also prevent photosynthesis by reducing nutrient absorption (Navarro, 2008). However bio-compatibility of NPs or nanocomposites should be examined thoroughly before application and then only this nanostrategy will emerge as bless rather being the boomerang.

4. GREEN OR ORGANO-MANUFACTURING OF NP AND NMS REDUCES ECO-TOXICITY

Green manufacturing of nanoparticles or materials can be possible with Phytonanotechnology or by clay polymer composite preparation. Synthesis of NPs through bio-reduction by clay or plants very much cost effective and can be used as alternative, economic, sustainable and valuable approach for large scale nano particle production. Extracts from plant or clay decoration of NPs act as both reducing and capping agent. The bioreduction of metal nano particle in combination with biomolecule like enzyme, organic acids, aminoacids polysaccharides are environmentally benign but having great chemical efficiency.

4.1 Phyto –Nanotechnology: Offers an Added Value To Eco-Manufacturing Of Nps

Phyto-nanotechnology has additive and stimulatory effect than using any single technology. Nanoparticles produced by plants is more stable and the rate of synthesis is faster than in the case of microorganisms. A possible route to the synthesis of metal nanoparticles is by biological production from vascular plants may occur in phytoextraction or phytomining (Brooks et al. 1998) and phytoremediation (Pilon-Smits 2005; Arthur et al. 2005). Metal nanoparticles in plants have been observed for gold (Anderson et al. 1998; Sharma et al. 2007; Gardea-Torresdey et al. 2002), silver (Harris and Bali 2008; Brown et al. 1962), copper (Manceau et al. 2008), and of an alloy of gold–silver–copper (Haverkampetal, 2007). The limit on metal nanoparticle accumulation is assumed to be controlled by the total reducing capacity of the plant for the reduction potential of the particular metal species reacting, the metal ion's oxidation state and this capacity partly depends on the electrochemical potential gradient to be established between them.

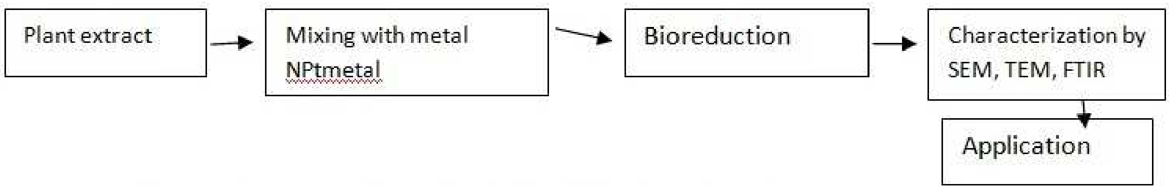


Figure 3: Nano particle synthesis in plant material (bottom up approach)

Nanofabrication with hyper-accumulator plant or in combination with soil microorganism provides the approach of "Designer plant" boosting up the nutrient uptake and phytomining efficiency. Biopolymer-stabilized iron nano-particles effectively degrade lindane. Moreover, nano-particles can affect the fate and uptake of organic pollutants in phytoremediation systems. For example, fullerenes enhance the uptake of trichloroethylene in *Populus deltoids*. CeO_2 and ZnO nanoparticles have increased root and shoot growth in edible plants such as soybean, wheat, corn and alfalfa suggesting that nanotechnology can significantly enhance the efficiency of phytoremediation.

4.2 Green Synthesis of Nps in Some Common Plants

Plant name	Plant part	Type of NPs
Calotropisgigantea	leaves	Ag
Polyalthiya longifolia	leaves	Ag
Solanum torvum	leaves	Ag
Turnera ulmifolia	leaves	Ag
Mangifera indica	leaves	Au
Murraya kennigii	leaves	Au
Corriandum sativum	leaves	Au

Nanoparticles in enzyme-based bioremediation can also be used in combination with phytoremediation. Polymer supported metal oxide/metal nanoparticles are finding wider applications in catalysis, bioseparation, drug delivery, and environmental remediation. Donnan membrane effect caused by the host materials may play a significant role deciding the effectiveness of the hybrid materials for the purpose.

4.3 Nano-Clay Production

Various types of clay minerals are used for that purpose. The Indian red soil (alfisol), lateritic soil (ultisol) are rich in kaolinite, Black soil (vertisol) is rich in montmorillonite and all these diversity provide couple of scopes for production of organo clay-NPs. We know that filler anisotropy, i.e. large length to diameter ratio (aspect ratio), is especially favourable in matrix reinforcement which is fulfilled by clay minerals. In clay minerals, there are various kinds of bonds being changed from one form to another through isomorphous substitution or insertion of small ions (Li^{+}), or by use of organic compounds. The way nano-decoration could rely on charge properties such as: density, origin, and nature of charges; intensity and degree of manifestation of charge in nanoscale; and the nature (geometry) and extent of the interface available for reaction. The most widely used clay in the synthesis of nanocomposite polymer is montmorillonite (MMT) which is the major constituent of bentonite. The replacement of magnesium ions in clay interlayer structure was carried out using concentrated copper sulfate solutions at elevated temperature. Copper ions were reduced to elemental copper at 400–600 °C using hydrogen as the reducing agent. Strong adhesion of copper nanoparticles to the vermiculite carrier makes this hybrid very stable and durable.

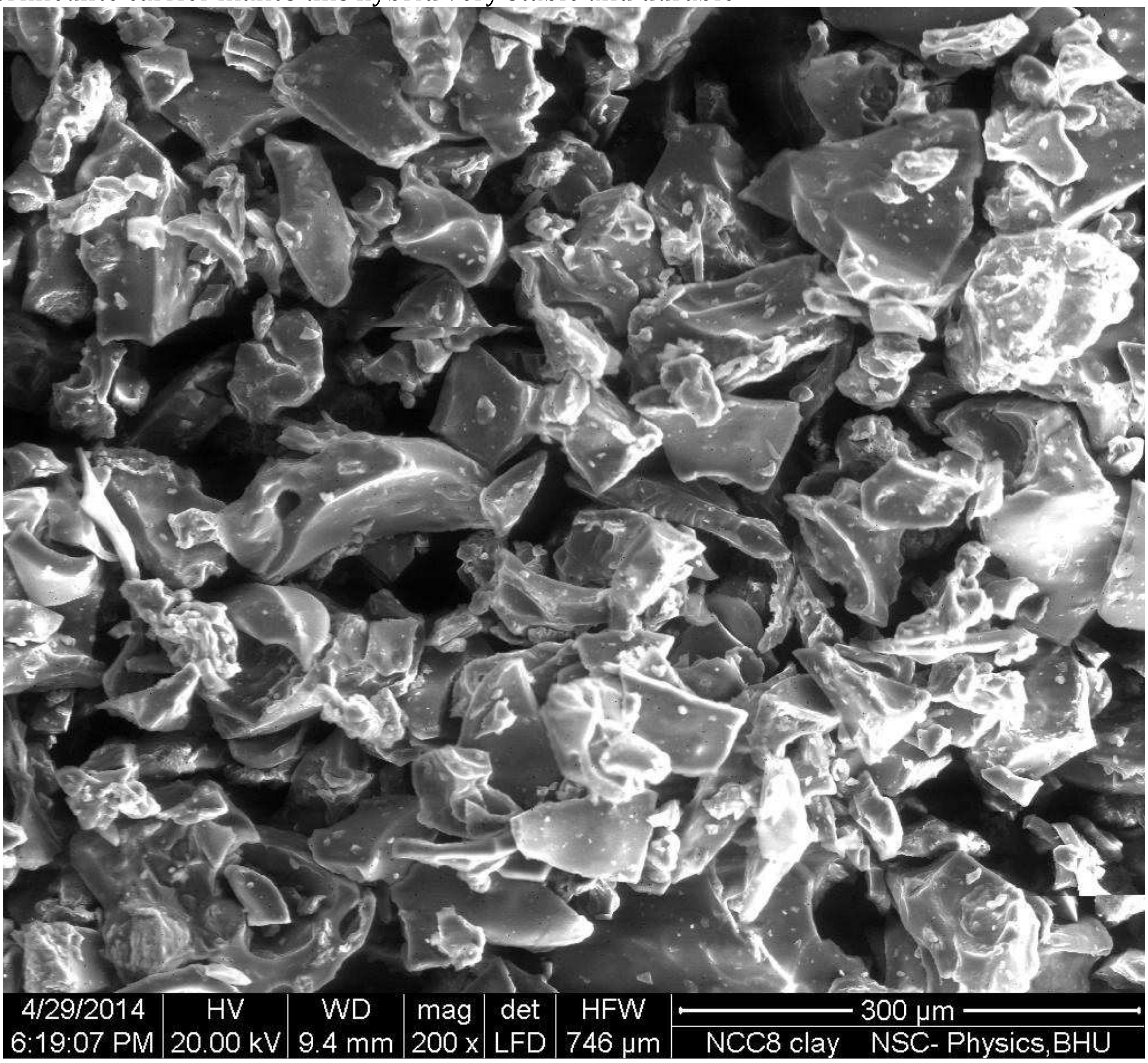


Fig 6: SEM of 1. Montmorillonite based nano-clay polymer

5. STATUS OF ADAPTATION OF THIS GREEN –TECHNOLOGY IN INDIA

Recent statistics suggests that 88% of the patents are generated from just seven countries comprising US, China, Germany, France, South Korea, Switzerland and Japan. But in India too this technology is flourishing day by day. Government of India has invested Rs.1000 crores through the Nano Mission Project during 11th Five Year Plan and the investment is likely to be several folds higher during the 12th Five Year Plan period. This nano-responsive budgeting obviously will inject a new flow in the development and exploitation of this novel mean. Development of nano-clay capsules are running under differe*nt* projects like under Pakistan-US Science and Technology Cooperative programme, TNAU nano-mission programme. In Tamil Nadu Agricultural University, a team has successfully encapsulated herbicide in a MnO_2 core shell shielded with bilayer polymers that open up and exuding the active ingredient on receipt of rainfall (Chinnamuthu *et al. 2010). This* method would save time and costs associated with tilling and manual picking. Primomax, Syngenta are several MNCs that are producing nano-emulsified PGRs. All these indicates that this innovative technology is though in seedling stage at present in India, soon it will take its pace through extensive research and commercialization and finally will revitalize the anemic agricultural growth with food safety and food security.

CONCLUSION

In spite of some loopholes, nano-integrated these technologies have several benefits that obviously weigh higher than its backdrops. Our research should focus on increasing the bio reactivity as well as well as improving the biocompatibility of nano encapsulated agrochemicals. Researches on critical plant diseases diagnosis and their control through nanotechnology should be equally addressed as it is utilized in animal drug delivery or disease control approaches. In our lab too the excellent competence of *Trichoderma* loaded clay was recorded and with these result and above discussion it can be assumed that in recent future nano-clay composite and green –manufactured NPs would be one of the most efficient key route to achieve growth, sustainability and speed up Indian agriculture in a positive way.

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